Effect of Heterogeneous Mechanisms During Reburning of Nitrogen Oxide

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NO reduction through heterogeneous mechanisms is a major concern when coal or lignite is used as reburning fuel. Reburning was simulated in an alumina flow reactor operated with a synthetic flue gas at a stoichiometric ratio of 1.1, at 1,100°C and with a residence time of approximately 0.2 s. Reburning fuels used include methane, one bituminous coal, two lignites, chars derived from the bituminous coal and two lignites, and the bituminous coal char impregnated with CaO. Reburning with chars indicates that heterogeneous mechanisms are more important than homogeneous mechanisms when lignites are used. This high reactivity renders lignite char an even more effective reburning fuel than the parent lignite, while char from the bituminous coal produces little activities at stoichiometric ratios above 0.75. Bituminous coal char impregnated with CaO demonstrates higher NO reduction efficiency than the original char. Effects of SR on NO reductions imply that oxygen atoms, required for the NO and HCN conversions in homogeneous mechanisms, are not required in heterogeneous mechanisms. In fact, they inhibit the surface NO reduction. The first-level kinetic analysis indicates that the surface area is not the only contributor to a remarkable increase in NO reduction of lignite char, and chars of different origins seem to follow different mechanisms or to have different controlling steps in the overall reaction scheme.

Introduction

The U.S. Clean Air Act Amendments of 1990 regulate that a single NO_x control technology is not likely to be sufficient for boilers in the ozone nonattainment areas. Reburning is an emerging three-stage combustion technology designed for the NO reduction by introducing a small amount of reburning fuel above the primary flame where the majority of NO is chemically reduced to nitrogen in this fuel-rich environment. The concept of reburning was first introduced by Wendt et al. (1973). Tests on a full-scale boiler at Mitsubishi Heavy Industries (Takahashi et al., 1983) showed over 50% reduction in NO_x.

Coals, including lignites, are an economical source of carbon required for NO reduction in the fuel-rich environment. Its effectiveness as a reburning fuel depends on two seemingly unfavorable factors. First, a fraction of the nitrogen in coal will be converted to NO in the reburning and burnout stages. Conversion of volatile nitrogen during reburning has been the objective of an earlier study (Burch et al., 1994). Second, while the homogeneous gas-phase NO reduction in the fuel-rich environment is relatively well understood (Miller and Bowman, 1989), NO reburning by chars of diverse origin and history has not been the major objective of a systematic investigation.

Our previous studies of simulated reburning with reactors of two scales (Burch et al., 1991a,b, 1994; Chen et al., 1991) have demonstrated that lignites are more effective than methane. The two lignites tested were selected from Mississippi and North Dakota; both lignites have high contents of calcium. Initial screening with the North Dakota lignite indicated that the lignite char surface participates in heterogeneous/catalytic NO reduction to HCN, while lignite ash enhances catalytic HCN reduction to NH_3. Both reactions are important in the overall NO reduction scheme. The effectiveness of lignite for NO reduction during reburning has recently been demonstrated in a 1.0 MBtu/h (293 kW) pilot-scale test facility (Payne et al., 1995).

Detailed kinetic analysis of homogeneous phase NO reduction in fuel rich environment indicates that the majority of

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NO is reduced by hydrocarbon radicals C, CH and CH_2 to HCN and amine radicals (NH_i) (Miller and Bowman, 1989). The amine radicals, in turn, can be converted to N_2 or NO. The yields of these desirable hydrocarbons radicals from lignite during reburning are not known. Nevertheless, coal and lignite produce only about 50% of the volatile carbons of that which methane produces at the same stoichiometry, which led to the speculation that the lignite char participates in considerable heterogeneous reactions with NO.

Although NO reburning by char has not been a major area of research, investigating the interactions of NO and carbonaceous materials has been the objective of a number of studies. An extensive review has been conducted by De Soete (1990). It has been shown that carbonaceous materials can be gasified by NO to form CO, CO_2 and N_2 (Bedjai et al., 1958; Smith et al., 1959; Furusawa et al., 1980; Levy et al., 1981; Chan et al., 1983; Suuberg et al., 1990; Teng et al., 1992; Chu and Schmidt, 1993; Illan-Gomez et al., 1993). The gasification reaction can be promoted by the addition of reducing agents, such as CO and H_2, and inhibited by O_2 when the CO_2/CO ratio is higher than one (De Soete, 1990). In addition to gasification, reaction of NO with CO on various surfaces, including char, ash and soot, can also be a major route of heterogeneous NO reduction mechanisms (De Soete, 1990). Catalytic decomposition of NO on various metallic oxides, some are common constituents in the lignite, has been reported by Winter (1971).

Huffman et al. (1990) reported that calcium is dispersed in coal macerals and is bonded to the oxygen anions. During combustion, the calcium present in lignite agglomerates, and eventually forms CaO and CaS. Recent lab-scale investigations of fluidized-bed combustion (FBC) and circulating FBC (CFBC) has shown that calcium sulfide (Hansen et al., 1992), CaO (Allen, 1991; Hansen et al., 1992; Hansen and Dam-Johansen, 1993; Shimizu et al., 1993; Lin et al., 1993) and Fe_2O_3 (Allen, 1991) serve as catalysts for NO reduction in various environments. While most of these researchers claimed that these catalysts enhanced the gasification or the conversion of NO + CO to form CO_2 and N_2, Lin et al. indicated that CO decreases the NH_3 conversion to NO. Lin et al. also claimed that NO may oxidize NH_3 to form nitrogen through homogeneous and heterogeneous mechanisms in FBC or CFBC. These char gasification and mineral-catalyzed reactions in reburning environments have not been fully investigated, but can certainly be enhanced by the highly porous nature of lignite char. The complexity of calcium-NO interactions has been demonstrated by infrared studies (Low and Yang, 1974; Allen, 1990).

The effects of calcium during oxidation of various solid carbonaceous materials has also been examined through a class of impregnation/ion-exchange techniques (Walker et al., 1979; Radovic et al., 1983; Hengel and Walker, 1984; Radovic et al., 1985; Levendis et al., 1989). In a study of the catalytic effects of ion-exchange of lignite on char oxidation, Walker et al. found that the reactivity of various calcium-containing chars in air, CO_2 and water vapor increased linearly with increasing calcium. Radovic et al. (1983) discovered that the well-dispersed calcium oxide formed upon pyrolysis of lignites is a very efficient *in-situ* catalyst for sulfur capture. The char reactivity decreases with the increasing severity of pyrolysis conditions which is probably due to CaO crystallite growth. Levendis et al. reported that carbon oxidation can be catalyzed by calcium up to two orders of magnitude.

Mild oxidation has been used to enhance the oxygen functional groups and the subsequent ion-exchange capability of carbonaceous materials (Chang et al., 1986). Following the same concept, Bartholomew et al. (1991) and Gopalakrishnan et al. (1994) produced char in the presence of oxygen and used the same ion-exchange/impregnation procedure discussed above. Their results indicate significant catalytic effects: up to a 160-fold increase for $CaCO_3$ catalysis, a 290-fold increase for $CaSO_4$, and up to 2,700 times for CaO.

While most of the studies in the literature have been centered around the Ca-catalyzed char oxidation by oxygen, Wojtowicz et al. (1991) reported that oxidation of a peat char by N_2O during FBC can be catalyzed by impregnating the char with CaO. Recently, Illan-Gomez et al. (1995) reported that calcium catalyzes NO-carbon reaction at 300 to 600°C through a mechanism that is consistent with the formation of intermediate CaO(O) surface species.

The primary objectives of this study are to improve the understanding of heterogeneous NO reduction mechanisms during reburning with coal and lignite. To isolate heterogeneous from homogeneous mechanisms, devolatilized chars are included in reburning experiments. The effect of surface area is investigated by comparing data with a Langmuir adsorption model. Possible catalytic effects have been examined through reburning with bituminous coal char impregnated with CaO. Finally, we discuss the potential impacts of this study on the reburning practice.

Experimental Studies

Reburning

The experiments reported here were carried out in a ceramic flow reactor (Burch et al., 1991a,b) with a simulated flue gas consisting of 16.8% CO_2, 1.95% O_2, and 0.1% NO in a helium base. Only reburning fuel, NO and two oxidants, are included in the simulated flue gas to investigate the effects of variables of primary importance. Reactants of secondary importance, such as H_2O, OH, H_2, and SO_2 are not included. These concentrations of CO_2, O_2, and NO were chosen to be consistent with those of a coal primary flame operated at a stoichiometric ratio of 1.1. Helium, instead of nitrogen, was used as the base gas to minimize heating time.

The flow reactor used for this research was an alumina tube (Coors Ceramics Co.) with 1.91 cm ID and overall length of 64 cm. The central portion of the reactor tube was enclosed in a 30-cm-long, electrically heated furnace (Lindberg Model 55035), which provided tube temperatures up to 1,150°C.

Furnace temperature profiles were determined by both centerline traverse and wall mounted type K thermocouples. These two methods agreed within ±5°C. The furnace produced a parabolic axial temperature profile with a relatively flat peak (±20°C) over approximately 20 cm of the heated length. Outside the zone of maximal heating, the temperature fell rapidly at a rate of approximately 60°C/cm. For typical flow conditions, this corresponds to heating and cooling rates on the order of 2,000°C/s. Furnace temperature profiles with and without combustion produced identical temperature profiles except for a narrow zone of maximum heat release where both wall mounted and centerline thermocouples exhibited an approximate 10°C rise.

The centerline temperature measurements were taken using a 0.32-cm-OD sheathed but unshielded thermocouple. Due to high radiation from the walls, the temperature profiles obtained by this method are more representative of the wall temperature than the mean gas temperature at any given location. Using property data for the simulated flue-gas composition, and the method of Sellars et al. (1956), the maximum gas temperature is estimated to be 50°C lower than the maximum wall temperature and to be maintained for only 10 cm of the furnace length. The estimated average gas temperature and reaction time for this 10-cm zone are the basis for the data analysis presented here.

This assignment of an accurate reaction temperature is complicated by the variety of fuels used. Variations in the required induction time may cause a fraction of the reaction to take place before the maximum gas temperature is reached. Since many of the radical species important in reburning are short-lived, the most appropriate reaction temperature may be somewhat lower than that reported.

All of the gas flows were measured individually with specifically calibrated rotameters. The gas mixtures, with certified composition, were purchased from Matheson Gas Products Inc., Liquid Air Corp., or Liquid Carbonic.

For experiments with coal as the reburning fuel, the delivery system was modified to incorporate a laboratory-scale coal feeder. Details of this device have been reported elsewhere (Burch et al., 1991b). Part of the gas flow (usually helium) was diverted through the coal feeder as a carrier gas.

The sampling train consisted of 0.635 cm, stainless steel transfer lines and a switching manifold with stainless steel valves. Transfer lines from the reactor tube exit to the impinger were heat traced (80°C) to minimize adsorption of HCN and NH_3. The effluent was desiccated with anhydrous calcium sulfate before transfer to the instrument package through 0.635-cm teflon tubing. For coal experiments, the sampling train was modified to allow the gaseous products (and particulate matter) to pass straight through the end of the reactor tube onto a paper filter before entering the transfer lines. The filter was enclosed in a glass housing and heated to 100°C. Recovery tests showed no loss of HCN or NH_3 in the filter. A 10-μm filter was also added upstream of the desiccant dryer for coal experiments. The flow reactor was maintained near atmospheric pressure by providing an atmospheric vent downstream of the instrument package and monitoring the supply gas pressure in the mixing chamber.

Fixed gas species of interest were monitored by an on-line instrument package. The analysis included NO_x (chemiluminescence, Thermoelectron), O_2 (paramagnetic, Beckman), CO and CO_2 (infrared, California Analytical Instruments). Differences between the base gas used for the calibration gas and sample gas were found to produce significant instrument error. This is particularly true for chemiluminescent NO_x measurement, which relies on a constant gas flow through capillary tubes. Thus each of these instruments was calibrated with a gas mixture representative of the feed gas composition.

HCN and NH_3 were collected by diverting the reactor effluent through a straight tube impinger filled with 0.5 L of 0.1N HNO_3 aqueous solution for a specified time interval. The captured solutions were pH adjusted with NaOH and analyzed for CN^- and dissolved ammonia with specific ion electrodes (Orion Research). Poisoning of the cyanide electrode by sulfur ions was prevented by adding an aqueous solution of $Pb(NO_3)_2$ prior to adding the NaOH. Sulfide ions were precipitated as PbS. Recovery of HCN and NH_3 by this method was tested using known standards and found to be near quantitative for NH_3, but only 22% for HCN (100 to 700 ppm of HCN). Thus, NH_3 values have been presented as measured while HCN values reported have been corrected for collection efficiency.

Coal analysis and char preparation

Lignites and bituminous coal were analyzed by Huffman Laboratory (Table 1).

Chars were prepared by lowering a sample basket into a 6.35-cm ID ceramic tube electrically heated by a split tube furnace (Thermcraft Model #23-18-12H). A 50 mesh stainless steel screen was installed as the distributor, which was located 6 in. (152 mm) high from the bottom of the furnace. To provide an effective heat transfer to the gas, a silicon sand layer was placed on the distributor. The coal/char basket assembly consisted of a stainless steel handle (1/4-in. stainless steel tubing) and a stainless steel basket (serving as the coal/char container, 2.2-cm OD × 15-cm height). The basket is equipped with a mesh screen cover.

During the pyrolysis, the sample basket, with only two-thirds of its volume filled with the sample (about 20 g), was lowered into the ceramic tube just above the sand bed. The volatile products were carried away by nitrogen. The set temperature of the furnace wall was then raised from the room temperature to 1,050°C with a 0.45°C/s heating rate. The temperature of the fluidizing sand below the sample basket reached only 950°C. Reburning of our study was conducted at 1,100°C, a temperature higher than the pyrolysis temperature 950°C. Review of coal pyrolysis literature (Howard, 1981) indicated that the chars derived from the Pittsburgh #8 coal and the Montana lignite produced only about 3% of additional volatiles (as received basis) due to a temperature increase from 950 to 1,050°C. Therefore, the char derived from the present study can be considered completely devolatilized, and the effects of volatiles generation and homogeneous phase NO reduction are negligible when these chars are used as reburning fuels. After the furnace reached the set temperature, the sample was kept in the furnace for another 5 min. Quenching was achieved by raising the sample basket to a

Table 1. Ultimate Analysis of Coal and Lignites*

Contents (%)	MS Lignite	ND Lignite	Pittsburgh #8 Bituminous Coal
Moisture	0.29	14.39	2.02
Carbon	53.07	60.63	70.48
Hydrogen	5.34	4.44	4.66
Oxygen, by Difference	16.32	22.63	8.53
Nitrogen	0.58	0.86	1.44
Sulfur	0.94	1.19	3.35
Ash	23.75	10.25	11.54

*Moisture was determined by loss on drying in air at 105°C for 1 h. All other results are reported on a dried sample basis.

Table 2. Ultimate Analysis of Chars*

Contents (%)	MS Lignite Char	ND Lignite Char	Pittsburgh #8 Bituminous Coal Char	Pittsburgh #8 Bituminous Coal Char Impregnated with CaO
Moisture	0.55	0.60	0.27	0.95
Carbon	56.54	78.49	80.43	79.78
Hydrogen	0.77	0.47	0.47	0.58
Oxygen, by Difference	0.0	0.0	0.0	0.0
Nitrogen	0.41	0.62	0.93	1.09
Sulfur	1.33	2.04	2.11	2.26
Ash	45.2	21.68	19.00	17.16
CaO			2.97	5.21

*Moisture was determined by loss on drying in air at 105°C for 1 h. Char results are reported on a dried sample basis. CaO is reported on an ash basis.

water-cooled, reversed-nitrogen gas flow section. The sample was kept in the quenching zone for about 20 min before being removed from the furnace. The char samples were stored in glass bottles sealed with caps. This procedure generates char with a weight percentage (on dry basis) for 49.6% of the Mississippi lignite, 55.7% for the North Dakota lignite, and 61.8% for Pittsburgh #8 bituminous coal. These chars were analyzed by the Huffman Laboratory (Table 2).

Impregnation

The impregnation and ion-exchange techniques follow that which were developed by Radovic et al. (1983, 1985). Char derived from the pyrolysis of bituminous coal was used for impregnation. Furthermore, a series of reburning experiments was conducted with char which was partially oxidized before impregnation to activate the possible oxygen complex required for calcium attachment. These procedures have been summarized in Figure 1. Slurry of 10-g char and 250 mL of 1.5-M calcium acetate aqueous solution was kept at room temperature for 24 h. The pH of the solution was adjusted to 8.5 by adding a few drops of 0.01-N solution of $Ca(OH)_2$ to enhance the possible ion-exchange with the oxygen-containing complexes in the char. The solution is then filtered, washed with 200-mL deionized water, and dried at 105°C for 12 h. Before reburning, the impregnated char is thermally treated to 900°C in nitrogen with the same furnace for the char production for about 5 min. With this treatment, the incorporated calcium acetate converts to $CaCO_3$ at 450°C, and then $CaCO_3$ converts to CaO at 775°C (Bartholomew et al., 1991). Reburning was conducted within 1 h after the thermal treatment to avoid formation of $CaCO_3$ through recombination of CaO with CO_2. For the preparation of partially oxidized char, the Pittsburgh #8 bituminous coal char was placed in a furnace at 300°C for 5 h before impregnation. The furnace was flushed with air during treatment. The char has the same CaO content as the coal (2.97%, on an ash basis), and the impregnated CaO loading is about 2.24% on an ash basis, or 0.43% on the char basis. Partial oxidation did not increase the calcium loading. This level of impregnation is much lower than that of lignite char reported by Gopalakrishnan et al. (1994), 2.8% on the char basis, which may be due to lower surface area of the bituminous coal char.

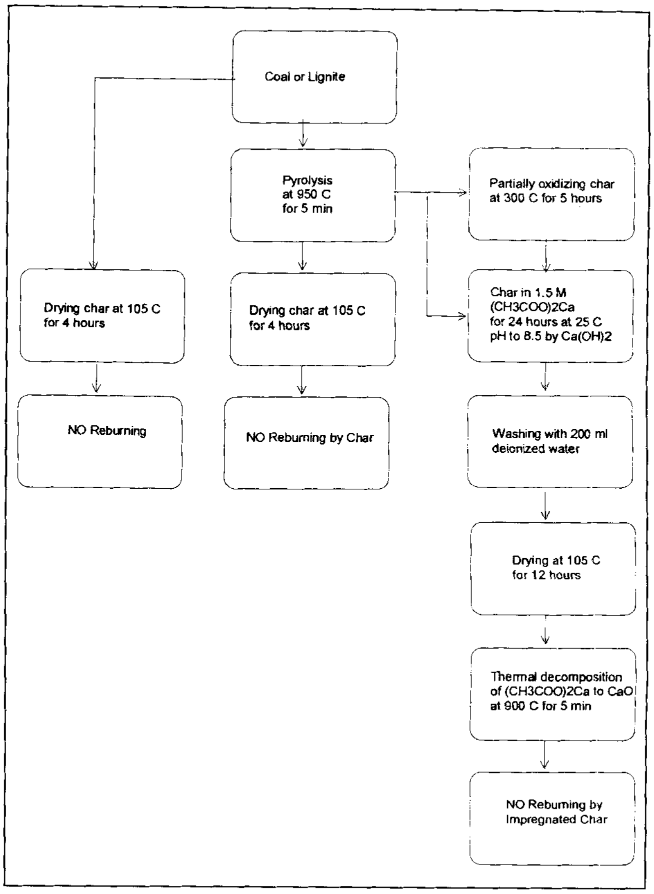

Figure 1. Experimental flow chart.

Results and Discussion

Figure 2 shows effects of reburning fuel and stoichiometric ratios (SR) on the yields of NO. Figures 3 and 4 present effects of these variables on the yields of two major intermediates, HCN, and NH_3, respectively. The results of reburning

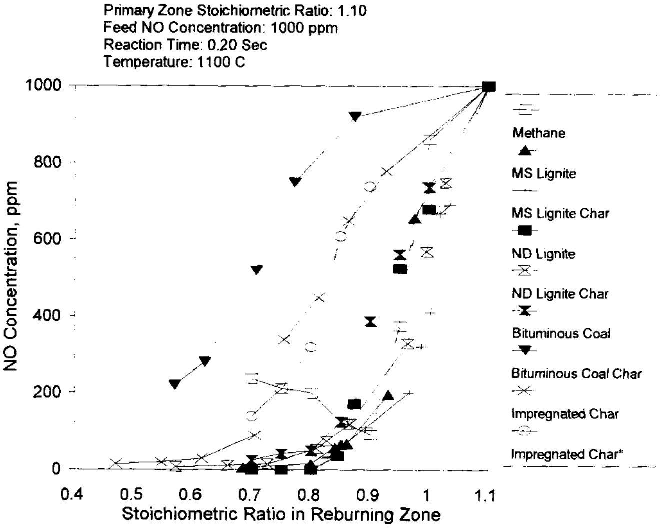

Figure 2. Effects of reburning fuels on exit NO concentrations.

*Partially oxidized char before impregnation.

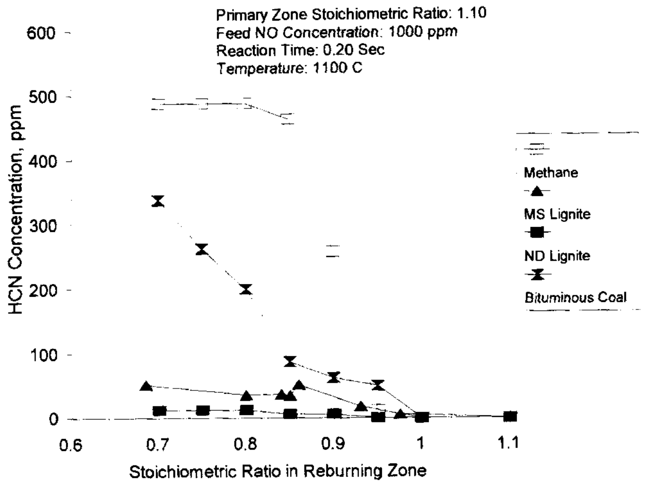

Figure 3. Effects of reburning fuels on exit HCN concentrations.

with methane have been extracted from an earlier study of ours (Burch et al., 1991b). Although North Dakota lignite and Pittsburgh #8 bituminous coal were also included in the earlier study, reburning with these two fuels has been conducted again for avoiding system peculiarity, and for comparison of chars with their parent coals.

Effects of reburning fuels on NO yields

Figure 2 indicates that lignite chars and lignites are the most effective reburning fuels in our studies. The lignite chars show NO conversions even higher than their parent lignites over a wide range of stoichiometric ratios. These results indicate lignite chars can be rigorously involved in heterogeneous/catalytic reactions in reburning, such as those discussed in the introductory section. On the contrary, the bituminous coal char exhibits activity at other extremes. It is a poorer reburning fuel than its parent coal; in fact, it is the poorest reburning fuel among all the reburning fuels studied.

It is interesting to note that, for most reburning fuels, the exit NO emissions monotonically decrease with the increasing quantity of fuels (Figure 2). Methane is the only exception among the fuels studied, which has a minimum yield at SR = 0.9. In an earlier study of ours (Burch et al., 1991b), optimum SR were also observed for two other volatile fuels, hexane and benzene. The difference in NO yields from reburning with volatile and lignites seems to distinguish the heterogeneous mechanisms from the homogeneous mechanisms. Myerson (1975) has postulated that gas-phase NO reduction requires oxygen radicals to initiate the chain reaction; therefore, NO reburning efficiency decreases when excessive volatile fuel is added. Figure 2 indicates that oxygen is not required when lignites and chars are used during reburning. The Langmuir–Hinshelwood models of NO reduction on the activated carbon in the literature (Smith et al., 1959; Sheppard, 1974; Beer et al., 1980; De Soete, 1990) have suggested that adsorption of NO is a rate limiting step and surface oxygen complex inhibits NO reduction. The results in Figure 2 are consistent with these models, and seem to indicate the importance of heterogeneous mechanisms during reburning with lignite.

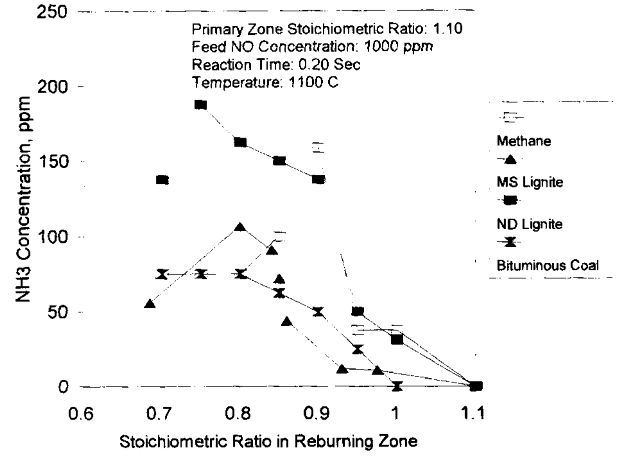

Figure 4. Effects of reburning fuels on exit NH_3 concentrations.

Figure 2 also shows that the NO reduction is enhanced by impregnating the Pittsburgh #8 coal char with CaO, though not to the levels of lignite. It should be mentioned that the ash of North Dakota lignite contains 23% CaO, while the ash of impregnated char contains only 5.21% CaO. The enhanced activity implies that the CaO-catalyzed char oxidation may be an important contributor to NO reduction during reburning with lignites.

Effects of reburning fuels on the yields of HCN, NH_3, and total fixed nitrogen

Due to the lack of hydrogen during reburning with chars, the yields of HCN and NH_3 are essentially zero and are not shown in Figures 3 and 4. The HCN yields from reburning with lignites are below 50 ppm at all stoichiometric ratios. Reburning with methane generates very high HCN yields, up to 500 ppm for SR < 0.9. This is also attributed by the lack of oxygen atoms required for HCN oxidation to NCO and NH (Miller et al., 1984).

Reburning with bituminous coal generated lower NH_3 yields than methane and lignites. The high HCN conversions to NH_3 observed in reburning with lignites seem to correlate the findings from pyrolysis of coals. Freihaut and Seery (1985) reported nitrogen distributions during lignite and coal pyrolysis with a flash-heated electric grid. Since very fine coal particles (−270+325 mesh) were employed under very low ambient pressure (0.001 torr), it was assumed that the mass-transfer limitations of volatile transport in the char particles and secondary reactions are minimal. Their data have indicated that distribution of nitrogen products, including HCN, tar nitrogen, and char nitrogen, varies significantly with the coal rank. For the wide range of coals studied, HCN, not NH_3, was the primary gaseous product. Only a very small portion of the coal nitrogen was converted to NH_3. Bose et al. (1988) demonstrated further that, under very short reaction times (< 1 s and 1 atm fuel-rich oxidative environment (SR = 0.6 ~ 0.8), NH_3 is derived from HCN and HCN from tar nitrogen. Their conclusion has been drawn for coals of various rank, including lignite. The ratio of NH_3 to HCN for lignite, however, increases with increasing reaction time and

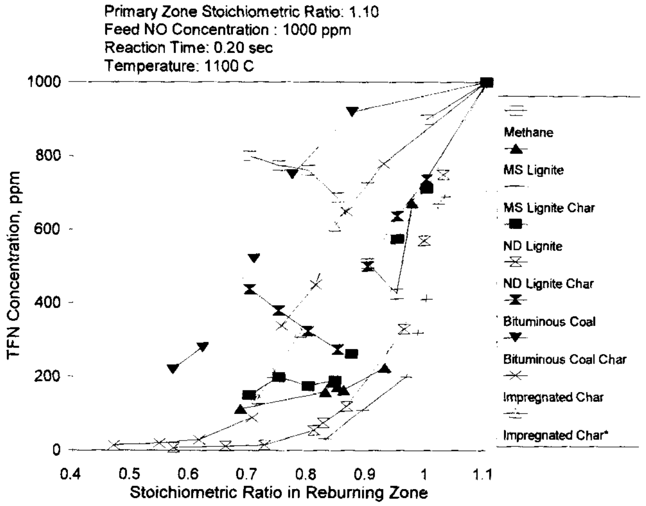

Figure 5. Effects of reburning fuels on total fixed nitrogen concentrations.

*Partially oxidized char before impregnation.

decreasing rank. In an earlier study of ours (Burch et al., 1991b), we have observed the catalytic reduction of HCN to NH_3 by lignite ash.

Figure 5 shows effects of reburning fuels on yields of total fixed nitrogen (TFN). Due to the extremely low yields of HCN and NH_3, lignite chars reburn very efficiently in terms of the total fixed nitrogen yields. For example, Mississippi lignite char achieves the same effectiveness at SR = 0.95 as the Mississippi lignite at SR = 0.90. Figure 5 also shows that the TFN yields from reburning with Mississippi lignite have almost the same values as those of the North Dakota lignite over a wide range of stoichiometric ratios. From the standpoint of TFN yields, the following order of effectiveness of fuels is observed in the practical range of stoichiometric ratios, from 0.80 to 0.90: lignite char > lignite > methane > bituminous coal > bituminous coal char impregnated with CaO > bituminous coal char.

Level of heterogeneous mechanisms

The results of reburning with chars have also been examined for their heterogeneous contributions. It was assumed that the coal or lignite consists of both char and volatiles. Volatile matter contributed to homogeneous phase NO reduction during reburning, while reburning with char reveals maximum heterogeneous phase NO reduction under no competition from volatiles. Therefore, when the NO reductions from char reburning are compared with those from coal and lignite reburning of equivalent char feeding rate (or SR), the contribution of the heterogeneous mechanisms is elucidated.

Figure 6 presents the contribution of heterogeneous mechanisms during reburning with Mississippi lignite based on the calibration discussed above. The abscissa represents reburning stoichiometric ratios with respect to Mississippi lignite, not its char. Similarly, Figures 7 and 8 present the heterogeneous contributions of NO reduction during reburning with the North Dakota lignite and the Pittsburgh #8 coal, respectively. Figures 6 and 7 indicate that the significant heterogeneous NO/char reactions during reburning with lignites are likely to have contributed higher NO reduction than the homogeneous mechanisms over a wide range of stoichiometries. For instance, at a stoichiometric ratio of 0.88, up to 65% of NO reduction could have been contributed by Mississippi lignite char. On the contrary, the char derived from the Pittsburgh #8 coal contributes negligible NO reduction when SR is greater than 0.75 (Figure 8).

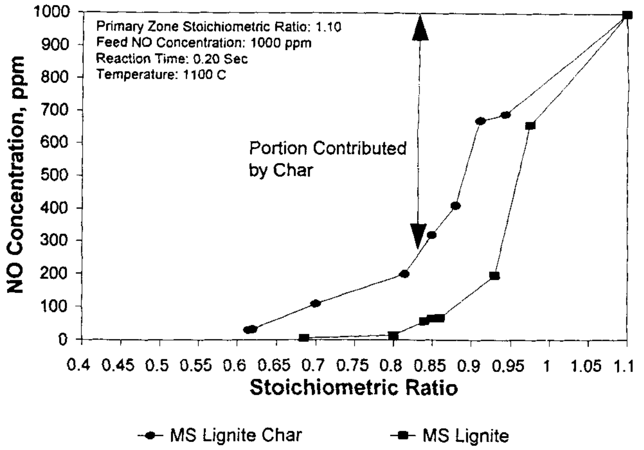

Figure 6. Heterogeneous vs. homogeneous reaction mechanisms during reburning with Mississippi lignite.

Implications of surface reactions

Resorting to a first level analysis discussed below, the data presented in Figures 6 and 8 imply that detailed analysis of surface reaction mechanisms is required for the fundamental understanding of NO reburning with lignite char. Assuming that internal and external mass transfers cannot be the major limiting steps in a system involving lignite char at 1,100°C

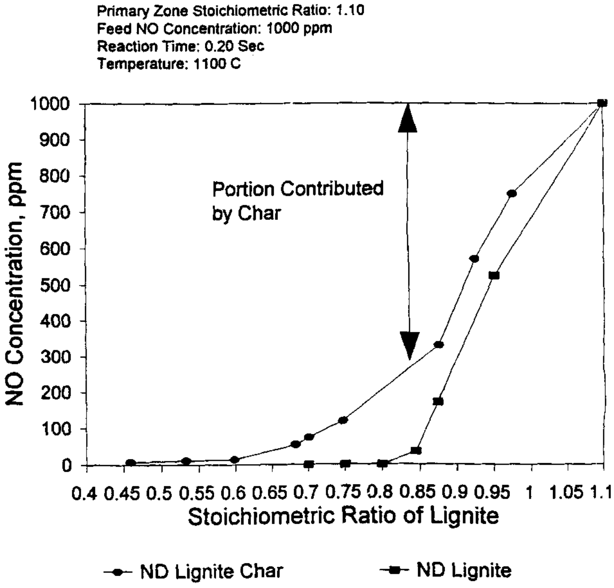

Figure 7. Heterogeneous vs. homogeneous reaction mechanisms during reburning with North Dakota lignite.

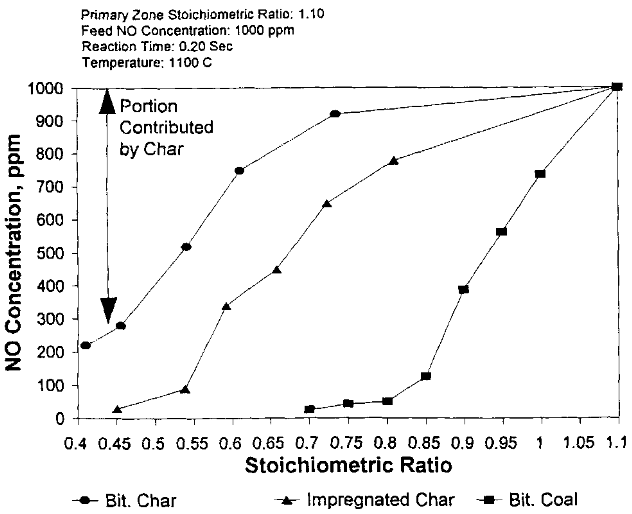

Figure 8. Heterogeneous vs. homogeneous reaction mechanisms during reburning with bituminous coal.

(Chen et al., 1994); thus, kinetic analysis should be focused on adsorption, desorption, and surface reaction mechanisms. For the NO reaction with char, a dual-site dissociative adsorption model (Beer et al., 1980; De Soete, 1990) results in the following Langmuir rate expression linearly proportional to surface area (i.e., total active sites), and to NO concentration when NO concentration is low.

$$-\frac{d(\mathrm{NO})}{dt}=\frac{kK_{\mathrm{NO}}P_{\mathrm{NO}}}{1+K_{\mathrm{NO}}P_{\mathrm{NO}}}$$

where P_{NO} is the partial NO pressure in the gas phase, k the rate constant, and K_{NO} the adsorption constant of NO on the solid. When the NO concentration in the feed is low, the equation above reduced to a simple first-order rate expression (Levy et al., 1981).

From our BET analysis in nitrogen, surface areas of chars after pyrolysis are 20.1 and 66.9 m^2/g for chars derived from bituminous coal and Mississippi lignite, respectively. Surface areas of chars after reburning at SR = 0.9 decrease to 11.9 and 44.1 m^2/g for chars derived from bituminous coal and Mississippi lignite, respectively. Assuming the NO reduction follows first-order rate expression, a fourfold increase in specific surface area causes fourfold increase in NO reduction rate, and cubic increase in NO conversion after reaction times t. This can be seem from the ratio of exit NO concentrations from reburning with two types of chars

$$\frac{\text{exit NO conc. after reburn with lignite char}}{\text{exit NO conc. after reburn with bituminous coal char}}$$

$$=\frac{e^{-4kt}}{e^{-kt}}=e^{-3kt}=(1-x)^3$$

where k is the Arrhenius rate constant based on specific surface area of char derived from the bituminous coal, and x is NO conversion from reburning with the bituminous coal char. Figures 6 and 8 indicate that the ratio of exit NO concentrations during reburning with chars derived from the two different origins is higher than the cubic relation in the above expression. For instance, NO conversion by char derived from bituminous coal at SR = 0.75 is 0.08 (Figure 8), and the NO yield caused by a fourfold increase in surface area should be $(1-0.08)^3=0.78$. Nevertheless, the NO concentrations from reburning with char derived from lignite at SR = 0.75 is only 0.18. This analysis suggests that surface area alone is not able to contribute to the high conversion observed from reburning with lignite char, and chars of different origins seem to follow different mechanisms or to have different controlling steps in the overall reaction scheme.

It is known that the N_2 at 77 K in BET measurement cannot penetrate into the micropores of chars and activated carbons (Mahajan and Walker, 1978; Yang, 1987). Alternatively, adsorption potential has been estimated based on capillary condensation of adsorbate, such as the Dubinin-Radushkevich (D-R) equation (Mahajan and Walker, 1978; Yang, 1987). Our analysis with the D-R equation and CO_2 as the adsorbate shows surface areas of chars after pyrolysis are 307.5 and 299.6 m^2/g for chars derived from bituminous coal and Mississippi lignite, respectively. Surface areas of chars after reburning at SR = 0.9 decrease to 228.5 and 199.9 m^2/g for chars derived from bituminous coal and Mississippi lignite, respectively. Since the difference in CO_2 surface areas between the two chars is not as large as the N_2 surface area, the conclusions about the impacts of factors other than surface area remain valid.

The observed decrease in surface areas of chars during reburning may be due to a structure ordering of carbon, or graphitization, taking place at elevated temperatures (Sahu et al., 1988; Wong et al., 1995). The structure reorganization of the carbon matrix at higher pyrolysis temperature up to 1,300°C leads to closure of pore mouths and pore coalescence, thus reducing surface area. Reburning of our study was conducted at 1,100°C, a temperature higher than the pyrolysis temperature 950°C.

Potential impacts on boiler performance

Our observation of the heterogeneous mechanisms along with the impregnation approach discussed herein may have profound impacts on the practice of coal-fired boilers in utilities and industries. First, if high NO reduction can be achieved by reburning with char at higher oxidant/fuel stoichiometric ratios, less unburned carbon will enter the burnout stage. This observation along with the demonstrated catalytic activity of calcium compounds in char oxidation, in turn, could lead to lower residual carbon and CO emissions which are typical concerns for a number of advanced NO control technologies. Second, previous studies (Pohl, 1976; Pershing and Wendt, 1979) have indicated that conversions of char nitrogen to NO is less than 50% of the conversion of volatile nitrogen. This indicates only a small fraction of the char nitrogen will be converted to NO in the burnout stage. Third, impregnation/ion-exchange technique is expected to increase the value of bituminous coal as a reburning fuel. Fourth, the presence of calcium compounds may also enhance sulfur capture, both in the reburning and in the burnout stages. Although SO_2 may compete with NO in the reburning zone for CaO, it has been established that CaS and $CaSO_4$ also catalyze the oxidation of char (Gopalakrishnan et al., 1994; Hansen et al., 1992).

Conclusions

Both Mississippi lignite and North Dakota lignite are effective reburning fuels. The chars derived from these lignites are even more effective than their parent coal. Heterogeneous mechanisms contribute more to NO reduction than homogeneous mechanisms over a wide range of stoichiometric ratios when Mississippi and North Dakota lignites are used as reburning fuels. The heterogeneous NO/char reactions during reburning with Pittsburgh #8 bituminous coal are essentially negligible when SR2 is greater than 0.75, which renders the bituminous coal to be a very poor reburning fuel. The effects of SR on the NO yields indicate oxygen is not required in heterogeneous NO reduction; in fact, oxygen inhibits the surface reaction.

A first level analysis indicates surface area is not the only contributor to the remarkable increase of NO reduction on lignite char, and chars of different origins seem to follow different mechanisms or to have different controlling steps in the overall reaction scheme. NO reduction by Pittsburgh #8 bituminous coal char during reburning can be improved by impregnating the bituminous coal char with CaO. Thus, CaO may also be an important contributor to the NO reburning with lignites.

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Literature Cited

Allen, D., "The Removal of Gaseous Pollutants during Coal Combustion," PhD Diss., Univ. of Cambridge, Cambridge, UK (1990).

Bartholomew, C. H., R. Gopalakrishnan, and M. Fullwood, "Catalysis of Char Gasification in O_2 by CaO and $CaCO_3$," Amer. Chem. Soc., preprint, Vol. 36, p. 982 (1991).

Bedjai, G., H. K. Orbach, and F. C. Riesenfeld, "Reaction of Nitric Oxide with Activated Carbon and Hydrogen," *Ind. Eng. Chem.*, **50**, 1165 (1958).

Beer, J. M., A. F. Sarofim, S. S. Sandhu, M. Andrei, D. Bachovchin, L. K. Chan, T. Z. Chaung, and A. M. Sprouse, "NO_x Emissions from Fluidized Coal Combustion," report to EPA, grant EPA/IERL-RTP #R804978020, Washington, DC (1980).

Bose, A. C., K. M. Danneker, and J. O. L. Wendt, "Coal Composition Effects on Mechanisms Governing the Destruction of NO and Other Nitrogenous Species During Fuel-Rich Combustion," *Energy Fuels*, **2**, 301 (1988).

Bradshaw, D. T., T. F. Butler, J. U. Watts, C. L. Howlett, and M. D. Lawley, "Micronized Coal Reburning for NO_x Control on a 175 Mwe Unit," *Proc. Joint ASME/IEEE Power Generation Conf.*, 93-JPGC-FACT-10 (Oct. 1-10, 1993).

Burch, T. E., R. B. Conway, and W. Y. Chen, "A Practical Pulverized Coal Feeder for Bench-Scale Combustion Requiring Low Feed Rates," *Rev. Sci. Instrum.*, **62**, 480 (1991a).

Burch, T. E., F. R. Tillman, W. Y. Chen, T. W. Lester, R. B. Conway, and A. M. Sterling, "Partitioning of Nitrogenous Species in the Fuel-Rich Stage of Reburning," *Energy Fuels*, **5**, 231 (1991b).

Burch, T. E., W. Y. Chen, T. W. Lester, and A. M. Sterling, "Interactions of Fuel Nitrogen with Nitric Oxide during Reburning with Coal," *Comb. Flame*, **98**, 391 (1994).

Chan, L. K., A. F. Sarofim, and J. M. Beer, "Kinetics of the NO-Char Reaction at Fluidized Bed Combustor Conditions," *Comb. Flame*, **52**, 37 (1983).

Chang, K. K., R. C. Flagan, G. R. Gavalas, and P. K. Sharma, "Combustion of Calcium-Exchanged Coals," *Fuel*, **65**, 75 (1986).

Chen, W. Y., T. W. Lester, L. M. Babcock, T. E. Burch, and F. R. Tillman, "Formation and Destruction of Nitrogen Oxides in Coal Combustion," final report to U.S. Dept. of Energy, DE-AC22-88PC88859, Pittsburgh (Nov., 1991).

Chen, W. Y., L. T. Fan, L. Ma, and M. Yashima, "Role of Char during Reburning of Nitrogen Oxide," Report submitted to U.S. DOE, grant DE-FG22-93PC93227 (July, 1994).

Chu, X., and L. D. Schmidt, "Intrinsic Rates of NO_x-Carbon Reactions," *Energy Fuels*, **32**, 1359 (1993).

De Soete, G. G., "Reduction of Nitric Oxide by Solid Particles," *Pulverized Coal Combustion: Pollutant Formation and Control: 1970-1980*, Beer et al., eds., EPA-600/8-90-049, Washington, DC (May, 1990).

Freihaut, J. D., and D. J. Seery, "A Phenomenological Understanding and Model of Fuel Bound Nitrogen Release in Coal Devolatilization and Pyrolysis," Int. Conf. on Coal Sci., Sidney, Australia, p. 957 (Oct., 1985).

Furusawa, T., D. Kunii, A. Oguma, and N. Yamada, "Rate of Reduction of Nitric Oxide by Char," *Int. Chem. Eng.*, **20**, 239 (1980).

Gopalakrishnan, R., M. J. Fullwood, and C. H. Bartholomew, "Catalysis of Char Oxidation by Calcium Minerals: Effects of Calcium Compound Chemistry on Intrinsic Reactivity of Doped Spherocarb and Zap Chars," *Energy Fuels*, **8**, 984 (1994).

Hansen, P. F. B., K. Dam-Johansen, J. E. Johnsson, and T. Hulgaard, "Catalytic Reduction of NO and N_2O on Limestone during Sulfur Capture under Fluidized Bed Combustion Conditions," *Chem. Eng. Sci.*, **47**, 2419 (1992).

Hansen, P. F. B., and K. Dam-Johansen, "Limestone Catalyzed Reduction of NO and N_2O under Fluidized Bed Combustion Conditions," *Proc. Int. Conf. on Fluid. Bed Comb.*, ASME, Vol. 2, p. 779 (1993).

Howard, J. B., "Fundamentals of Coal Pyrolysis and Hydropyrolysis," *Chemistry of Coal Utilization, Secondary Supplementary Volume*, M. A. Elliot, ed., Wiley, New York, p. 665 (1981).

Hengel, T. D., and P. L. Walker, "Catalysis of Lignite Char Gasification by Exchangeable Calcium and Magnesium," *Fuel*, **63**, 1214 (1984).

Huffman, G. P., F. E. Huggins, N. Shah, and A. Shah, "Behavior of Basic Elements during Coal Combustion," *Prog. Energy Comb. Sci.*, **16**, 243 (1990).

Illan-Gomez, M. J., A. Linares-Solano, L. R. Radovic, C. Salinas-Martinez de Lecea, and J. M. Calo, "NO Reduction by Activated Carbons: 1. The Role of Carbon Porosity and Surface Area," *Energy Fuels*, **7**, 146 (1993).

Illan-Gomez, M. J., A. Linares-Solano, L. R. Radovic, and C. Salinas-Martinez de Lecea, "NO Reduction by Activated Carbons: 4. Catalysis by Calcium," *Energy Fuels*, **9**, 112 (1995).

Levendis, Y. A., S. W. Nam, M. Lowenberg, R. C. Flagan, and G. R. Gavalas, "Catalysis of the Combustion of Synthetic Char Particles by Various Forms of Calcium Additives," *Energy Fuels*, **3**, 28 (1989).

Levy, J. M., L. K. Chan, A. F. Sarofim, and J. M. Beer, "NO/Char Reactions at Pulverized Coal Flame Conditions," *Int. Symp. on Comb.*, Comb. Inst., p. 111 (1981).

Lin, W., J. E. Johnsson, K. Dam-Johansen, and C. M. Van den Bleek, "Interactions between NO_x Emission and Desulfurization in FBC," *Proc. of Int. Conf. on Fluid. Bed Combust.*, ASME, Vol. 2, p. 1093 (1993).

Low, M. J. D., and R. T. Yang, "Reactions of Gaseous Pollutants with Solids: V. Infrared Study of the Sorption of NO on CaO," *J. Cat.*, **34**, 479 (1974).

Mahajan, O. P., and P. L. Walker, "Porosity of Coals and Coal Products," *Analytical Methods for Coal and Coal Products*, Vol. 1, C. Karr, ed., Academic Press, New York, p. 125 (1978).

Miller, J. A., and C. T. Bowman, "Mechanism and Modeling of Nitrogen Chemistry in Combustion," *Prog. Energy & Comb. Sci.*, **15**, 287 (1989).

Miller, J. A., M. C. Branch, W. J. McLean, D. W. Chandler, M. D. Smooke, and R. J. Kee, "The Conversion of HCN to NO and N_2 in H_2-O_2-HCN-Ar Flames at Low Pressure," *Int. Symp. on Combustion*, Comb. Inst., p. 673 (1984).

Myerson, A. L., "The Reduction of Nitric Oxide in Simulated Combustion Effluents by Hydrogen-Oxygen Mixture," *Int. Symp. on Combustion*, Combustion Inst., p. 1085 (1975).

Payne, R., D. K. Moyeda, P. Maly, T. Glavicic, and B. Weber, "The Use of Pulverized Coal and Coal-Water-Slurry in Reburning NO_x

Control," *Proc. EPRI/EPA Joint Symp. on Stationary Combustion NO_x Control*, Book 4, Kansas City, MO (May 16–19, 1995).

Pershing, D. W., and J. O. L. Wendt, "Relative Contributions of Volatile Nitrogen and Char Nitrogen to NO_x Emissions from Pulverized Coal Flames," *Ind. Eng. Chem., Process Des. Dev.*, **18**, 60 (1979).

Pohl, J. H., "Fate of Coal Nitrogen," PhD Diss., Mass. Inst. of Technol., Boston (June, 1976).

Radovic, L. R., P. L. Walker, Jr., and R. G. Jenkins, "Importance of Catalyst Dispersion in the Gasification of Lignite Chars," *J. of Cat.*, **82**, 382 (1983).

Radovic, L. R., K. Steczko, P. L. Walker, Jr., and R. G. Jenkins, "Combined Effects of Inorganic Constituents and Pyrolysis Conditions on the Gasification Reactivity of Coal Chars," *Fuel Processing Technol.*, **10**, 311 (1985).

Sahu, R., Y. A. Levendis, R. C. Flagan, and G. R. Gavalas, "Physical Properties and Oxidation Rates of Chars from Three Bituminous Coals," *Fuel*, **67**, 275 (1988).

Sellars, J. R., M. Tribus, and J. S. Klein, "Heat Transfer to Laminar Flow in a Round Tube or Flat Conduit-Graetz Problem Extended," *Trans. ASME*, **78**, 441 (1956).

Sheppard, W. M., "A Kinetic Study of the Reaction of Nitric Oxide and Activated Carbon," PhD Diss., Clemson Univ., Clemson, SC (1974).

Shimizu, T., D. Fujita, K. Ishizu, S. Kobayashi, and M. Inagaki, "Effects of Limestone Feed on Emissions of NO_x and N_2O from a Circulating Fluid Bed Combustor," *Proc. Int. Conf. on Fluid. Bed Combust.*, Vol. 1, ASME, p. 611 (1993).

Smith, R. N., J. Swinehart, and D. Lesnini, "The Oxidation of Carbon by Nitric Oxide," *J. Phys. Chem.*, **63**, 544 (1959).

Suuberg, E. M., H. Teng, and J. M. Calo, "Studies on the Kinetics and Mechanism of the Reaction of NO with Carbon," *Int. Symp. on Comb.* Comb. Inst., Pittsburgh, PA, p. 1199 (1990).

Takahashi, Y., M. Sakai, T. Kunimoto, S. Ohme, H. Haneda, T. Kawamura, and S. Kaneko, "Development of MACT In-Furnace NO_x Removal Process for Steam Generators," *Proc. 1982 Joint Symp. Stationary Combust. NO_x Control*, Vol. 1, EPRI Report No. CS-3182 (1983).

Teng, H., E. M. Suuberg, and J. M. Calo, "Studies on the Reduction of Nitric Oxide by Carbon: The NO-Carbon Gasification Reaction," *Energy Fuels*, **6**, 398 (1992).

Walker, Jr., P. L., O. P. Mahajan, and M. Komatsu, "Catalysis of Lignite Char Gasification by Various Exchanged Cations—Dependence of Activity on Reactive Atmosphere," *Amer. Chem. Soc.*, preprint, **24**(3), 10 (1979).

Wendt, J. O. L., C. V. Sternling, and M. A. Matovich, "Reduction of Sulfur Trioxide and Nitrogen Oxides by Secondary Fuel Injection," *Int. Symp. Comb.*, Comb. Inst., Pittsburgh, PA, p. 897 (1973).

Winter, E. R. S., "The Catalytic Decomposition of Nitric Oxide by Metallic Oxides," *J. Cat.*, **22**, 158 (1971).

Wojtowicz, M. A., J. R. Pels, and J. A. Moulijn, "Solid-Catalysed N_2O Destruction in Combustion of Coal," *Proc. of Int. Conf. on Coal Sci.*, IEA Coal Res., Newcastle-upon-Tyne, p. 452 (1991).

Wong, B. A., G. R. Gavalas, and R. C. Flagan, "Effects of Char Formation Temperature on the Densification of a Bituminous Coal Char during Gasification," *Energy Fuels*, **9**, 493 (1995).

Yang, Y. T., *Gas Separation by Adsorption Processes*, Butterworths, Boston, p. 39 (1987).

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